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Development of High Efficiency Segmented Thermoelectric Unicouples

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Abstract

Highly efficient, segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit are currently being developed at the Jet Propulsion Laboratory (JPL). These segmented unicouples include a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. The maximum predicted thermal to electrical efficiency is about 15% for a hot-side temperature of 975K and a cold-side temperature of about 300K. Various segmentations have been explored and several unicouples have been fabricated and tested. The set-up for testing these unicouples is described in this paper and some of the tests results reported. I-V curves have been generated for selected unicouples. The results show that experimental thermal to electrical efficiency values close to theoretical predicted values have been measured.

Introduction

A segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit has been under development at the Jet Propulsion Laboratory (JPL) under the sponsorship of the U. S. Defense Advanced Research Projects Agency (DARPA) since 1997 [1-5]. This advanced segmented thermoelectric unicouple includes a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel materials developed at JPL. The optimal version of these segmented unicouples has a projected thermal to electrical efficiency of up to 15 % when operating at a cold-side temperature of 300K and a hot-side temperature 975K. The segmentation can be adjusted to accommodate various hot-side temperatures depending on the specific application envisioned. The segmented unicouple under development incorporates a combination of state-of-the-art thermoelectric materials and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. The segmented unicouple is illustrated in Figure 1. A semi-analytical approach based on the Swanson's model [6] has been used to optimize and calculate the expected properties of the device. Some details of the model have been reported earlier [1-3].

The model can calculate (based on the measured thermoelectric properties of the materials as a function of temperature) the optimal lengths of the segments, the ratio of the cross sectional area between the n-type and p-type legs, the internal resistance, the power output, I-V curve, and thermal to electrical efficiency as a function of hot side and cold side temperatures. In addition, electrical contact resistances between the segments and at the hot and cold interconnects can be taken into account by the model. The calculated thermal to electrical efficiency values are shown in Figure 2 as a function of hot and cold side temperatures. These values assumed no electrical contact resistance at the various interfaces in the unicouple.

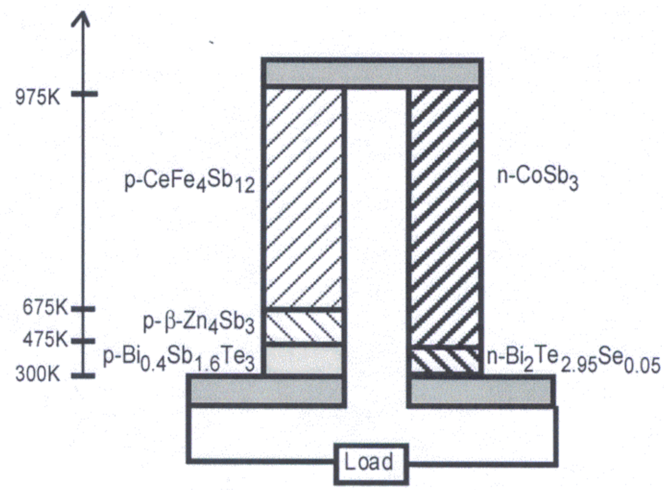

Figure 1. Illustration of the advanced, segmented unicouple incorporating new high performance thermoelectric materials. The relative lengths of each segment and the cross-sectional areas for the p- and n-legs are drawn to scale. The maximum calculated thermal to electrical efficiency is about 15%.

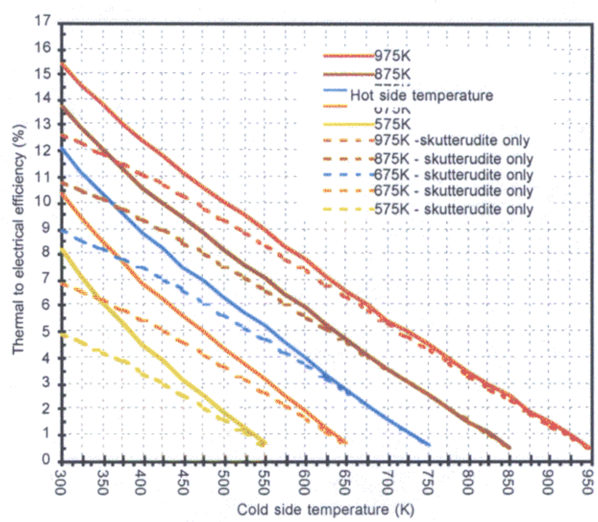

Figure 2. Calculated thermal to electrical efficiency values for 2 different versions of the advanced unicouple: 1) fully segmented version as illustrated in Figure 1 (solid lines) 2) skutterudite only legs as illustrated in Figure 3 (dashed lines). The maximum calculated thermoelectric efficiency is about 15%.

The maximum predicted thermal to electrical efficiency is about 15% for the fully segmented unicouple and for a cold and hot side temperatures of 300 and 975K, respectively. Calculations have been performed for two different type of unicouples: 1) a fully segmented version as depicted in Figure 1 2) a unicouple made of skutterudite-only legs (see illustration in Figure 3). The major impact of the addition of Zn_4Sb_3 and Bi_2Te_3-based segments to the unicouple on the efficiency is clearly for lower cold-side temperatures. As the cold side temperature increases, the contribution of the lower segments to the overall thermal to electrical efficiency becomes smaller. Keeping the cold side temperature around room temperature may not be realistic in some actual systems and a skutterudite only unicouple may be of interest for some applications. The maximum thermal to electrical efficiency achievable for a skutterudite only unicouple operating at a hot-side temperature of 975K and a cold side temperature of 375K is about 11.5%.

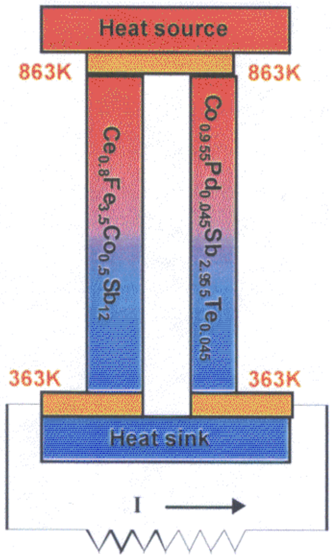

Figure 3. Illustration of an advanced unicouple incorporating skutterudite materials only.

Unicouple fabrication

Several versions of these unicouples are under development at JPL. In the following, the fabrication and testing of a unicouple made only from skutterudite materials is described and discussed. The entire thermoelectric legs were fabricated by hot-pressing pre-synthesized powders of p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys into cylindrical samples typically about 12 mm in diameter. The hot-pressing was conducted in graphite dies under Ar atmosphere. The samples can then be diced into legs of various dimensions using a diamond saw (Figure 4). The electrical contact resistance between the skutterudite materials and the metallic contacts was measured by a technique described earlier [3] and was found to be below 5 $\mu\Omega cm^2$. Typical variations of the electrical resistance as a function of distance of the skutterudite/metal junction are illustrated in Figure 5 for a p-type $Ce_{0.85}Fe_{3.5}Co_{0.5}Sb_{12}$/Ti junction. The results show that there is no increase of the electrical contact resistance when crossing the $Ce_{0.85}Fe_{3.5}Co_{0.5}Sb_{12}$/Ti junction.

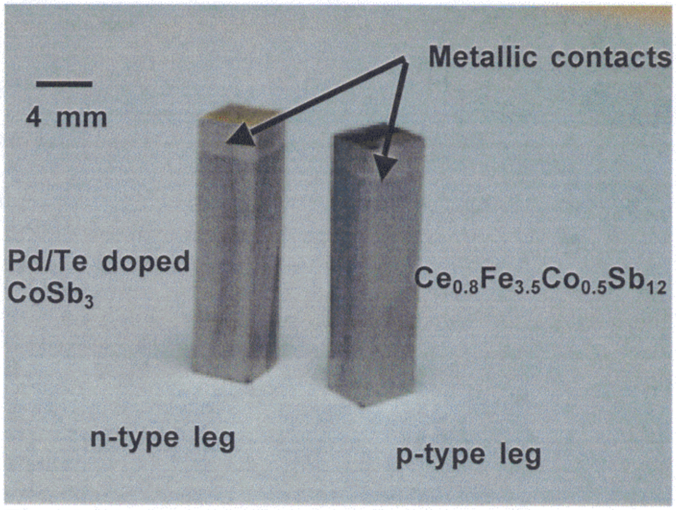

Figure 4. N- and p-type skutterudite thermoelectric legs with metallic contacts on the top.

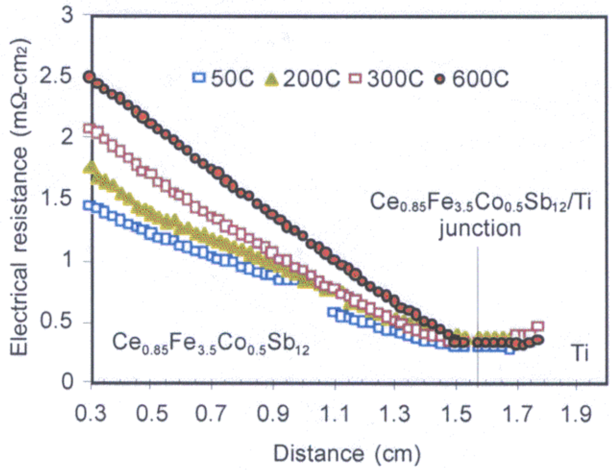

Figure 5. Electrical contact resistance as a function of distance for a $Ce_{0.85}Fe_{3.5}Co_{0.5}Sb_{12}$/Ti leg.

To perform thermal and electrical tests of the unicouple, it was built as follows. The lower ends of the legs were soldered using a Bi-Sn solder to large Cu blocks (Cu (1)s, Figure 6) which themselves were soldered to a Cu plated Al2O3 plate. The Cu layer (~100mm) plated on both side of the alumina was etched away in the center portion between the p- a and n-legs to insulate them electrically on the cold side. The alumina plate was soldered to a large Cu plate (Cu (2), Figure 6).

During the test, this Cu plate was water cooled in order to keep the bottom of the thermoelectric legs as cold as possible. The cold side temperature was recorded by thermocouples (500 μm in diameter) inserted in Cu blocks (Cu(1)s), just below the ends of the skutterudite legs. The hot-side temperatures in the p- and n-legs was recorded by thermocouples inserted in the metallic segments on the top of the legs. The electrical interconnect between the n- and p-legs on the hot side was fabricated by brazing a Nb metal bridge to the metallic ends of the n- and p-legs. All electrical contact resistances between the various contact interfaces were measured at the projected operation temperatures and were found to be below 5 $\mu\Omega cm^2$.

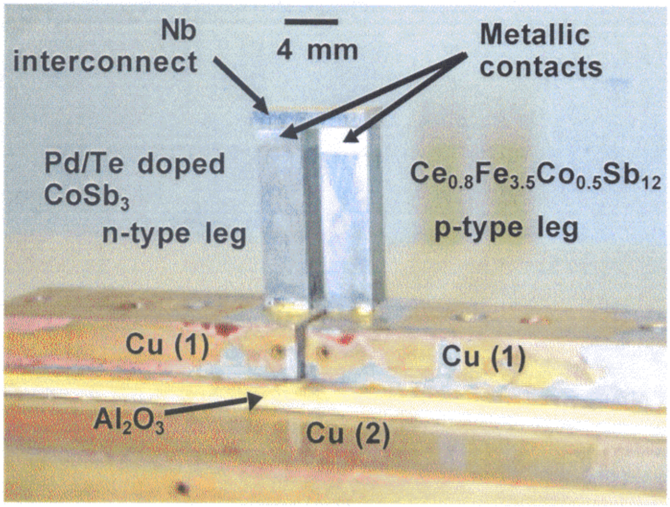

Figure 6. Fabricated unicouple (legs are 4 x 4 x 15 mm).

Figure 7 shows the unicouple instrumented in the test station. A W heating element was used to keep the hot side of the unicouple between 875 and 975K during the test. A slight pressure was applied to the heater using a spring-loaded bar to allow for thermal expansion at high temperatures. The assembly was then placed into a vacuum chamber and a Mo heat shield (made out of a 100 μm Mo foil) was placed around the unicouple to minimize heat losses by radiation. I-V curves were then generated and compared to predicted model values. Hot and cold side temperatures were monitored using thermocouples located inside the Cu blocks under the p- and n-legs (see Figure 6).

Results and discussion

The I-V curve is shown in Figure 8 for a unicouple made from skutterudite materials only. The cross sectional area for the p- and n-legs was about 0.6 cm^2 and both legs were approximately 1.5 cm long. The measured cold side and hot side temperatures during the test were 363 and 863K, respectively. The open circuit voltage was about 172 mV. This is in good agreement with a predicted value of 175 mV considering an estimated error of about 1% on the measure thermoelectric properties of the materials used for the calculation. The calculated unicouple internal resistance was 5.30 mΩ. The experimental internal resistance, determined for the variations of the measured unicouple voltage as a function of current, is 5.46 mΩ. This confirms that very low electrical contact resistances were achieved for all interfaces of the unicouple. The voltage decreases with increasing current and the maximum power output is achieved for half the value of the open circuit voltage. The maximum power output was 1.3 W at a current of about 15 A.

The results were compared to the predicted values (solid lines in Figure 8). The theoretical and experimental values for the voltage and power output are within a few %. The results demonstrate that the maximum experimental efficiency of the unicouple is about 10% for a hot-side temperature of 873K and a cold-side temperature of 363K. This constitutes the first experimental evidence of the high thermal to electrical efficiency of these advanced unicouples. To date, another skutterudite only unicouple has been operating for 13 days without any noticeable performance degradation.

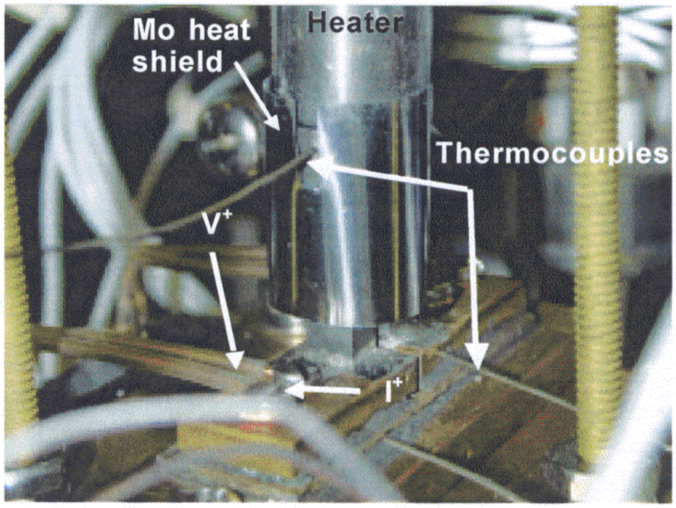

Figure 7. Unicouple shown in test station.

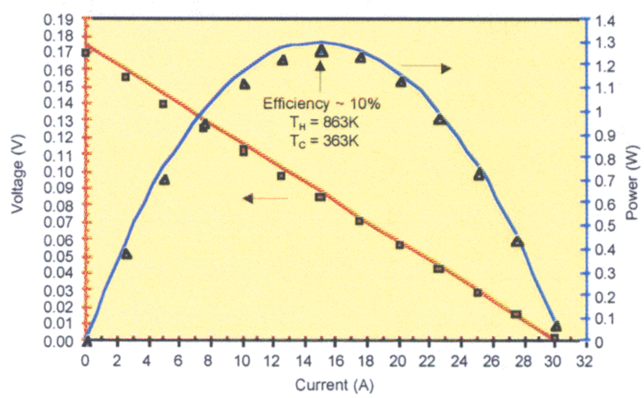

Figure 8. Theoretical (solid lines) and experimental (symbols) I-V curves and power output as a function of current for a skutterudite only unicouple. The maximum experimental efficiency obtained is about 10% for a hot-side temperature of 863K and a cold-side temperature of 363K, in good agreement with performance model predictions.

Life tests will be performed to identify possible degradation mechanisms including thermoelectric materials sublimation and mechanical failure. In addition, efforts should be made to design a testing procedure allowing for a system efficiency measurement, i.e. determining the efficiency by the ratio of heat input to power output. This will require a careful insulation of the unicouple to reduce heat losses, mostly by radiation, to a minimum. These initial results suggest however that these unicouples could be employed in thermoelectric generators for a variety of applications. Other versions of segmented unicouples designed for different hot-side temperatures are being developed and tested at JPL and it is expected that thermal to electrical efficiency values of up to 15% will be achieved in the near future, further expanding the possible range of applications.

Conclusion

Initial experimental results of the fabrication and testing of advanced thermoelectric unicouples were presented. The results show that experimental efficiency values on the order of 10% were achieved, in good agreement with theoretical predictions for the specific unicouple tested. Various unicouples are currently being developed and the maximum achievable efficiency is about 15%. While much development work remains to be performed before these unicouples can be used in actual thermoelectric generators, these initial results suggests that they might be useful high efficiency devices for a variety of applications including waste heat recovery and space applications.

Acknowledgments

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References

1. Caillat, T., Borshchevsky, A., and Fleurial, J. -P., "Development of High Efficiency Thermoelectric Generators Using Advanced Materials", in *Proceedings of the 15th Symposium on Space Nuclear Power and Propulsion*, edited by M. S. El-Genk editor, AIP Conference Proceedings 420, New York, USA, 1998, pp. 1647-1651.
2. Caillat, T., Fleurial, J. -P. , Snyder, G. J., Zoltan, A., Zoltan, D., and Borshchevsky, A., "Progress in the Development of High Efficiency Segmented Thermoelectric Generators", in *Proceedings of the 16th Symposium on Space Nuclear Power and Propulsion*, AIP Conference Proceedings 458, edited by M. S. El-Genk, New York, 1999a, pp. 1403-1408.
3. Caillat, T., Fleurial, J. -P. , Snyder, G. J., Zoltan, A., Zoltan, D., and Borshchevsky, A., "Development of a High Efficiency Segmented Thermoelectric Unicouple for Power Generation Applications", in *Proceeding of 18th International Conference on Thermoelectrics, Proceedings of the XVII International Conference on Thermoelectrics,* Baltimore, USA, IEEE Catalog Number 99TH8407, 1999b, pp. 473-476.
4. Fleurial, J. -P., A. Borshchevsky, A., and Caillat, T., "New Thermoelectric Materials and Devices for Terrestrial Power Generators", in *Proceedings of the 1st Conference on Synergistic Power and Propulsion Systems Technology*, edited by M. S. El-Genk, AIP Conference Proceedings 387, American Institute of Physics, New York, 1997a, pp. 293-298.
5. Fleurial, J. -P., A. Borshchevsky, A., Caillat, T., and Ewell, R., "New Materials and Devices for Thermoelectric Applications",in *Proceedings of the 32nd Intersociety Energy conversion Engineering Conference*, American Institute of Chemical Engineers, New York, 1997b, pp. 1080-1085.
6. Swanson, B. W., Somers, E. V., and Heike, R. R., " Optimization of the Sandwiched Thermoelectric Device" *Journal of Heat Transfer*, 77 (1961).